

# Rheology of Poly(ethylene oxide)/Clay Solutions

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## INTRODUCTION

Organic-inorganic nanocomposite materials have attracted significant interests recently because they exhibit synergistic behavior derived from the two components. Unique or enhanced mechanical, electrical, optical or thermal properties have been observed for both bulk and solution nanocomposites.

Inorganic clay has been widely used in applications such as drilling fluids, paints, cosmetics and pharmaceutical formulations. Their large aspect ratios may lead to supramolecular organizations and orientation under shear when mixed with polymers. Poly(ethylene oxide) (PEO) and a synthetic hectorite type clay, laponite, form viscoelastic solutions where both polymer and clay are well dispersed in water. Above a certain concentration the polymer/clay solution forms a dynamic network through the adsorption/desorption of polymer and clay platelets.<sup>1,2</sup> The dynamics of reversible networks, such as those formed by physically associating polymers, have been studied both theoretically and experimentally.<sup>3,4</sup> The current work focuses on understanding the dynamics of PEO/clay solutions.

## EXPERIMENTAL

Laponite (LRD) with a diameter of 300 Å and thickness of approximately 10 Å<sup>5</sup> was provided by Laporte Industries Ltd.\* Poly(ethylene-oxide) with a molecular mass of 10<sup>6</sup> g/mol was purchased from Polysciences Inc. NaOH and NaCl were purchased from Aldrich. All reagents were used as received.

The samples were prepared by dissolving PEO (mass fraction of 2 %) and LRD (mass fraction of 0 % to 3.5 %) in distilled deionized water with pH and ionic strength of 10 and 10<sup>-3</sup> respectively adjusted using NaOH and NaCl. The samples were hand mixed in a vial for several minutes a day followed by centrifuge for 30 min over at least three weeks. All samples were homogeneous and isotropic prior to measurement.

Rheological measurements were performed at 20 °C on a Rheometric Scientific ARES instrument with a parallel plate geometry (50 mm diameter). A fresh sample was used for each measurement. Since this rheometer has no solvent trap, solvent evaporation had to be taken into account after 1000 s. Duplicate experiments showed excellent reproducibility with relative standard uncertainty of 8 %.

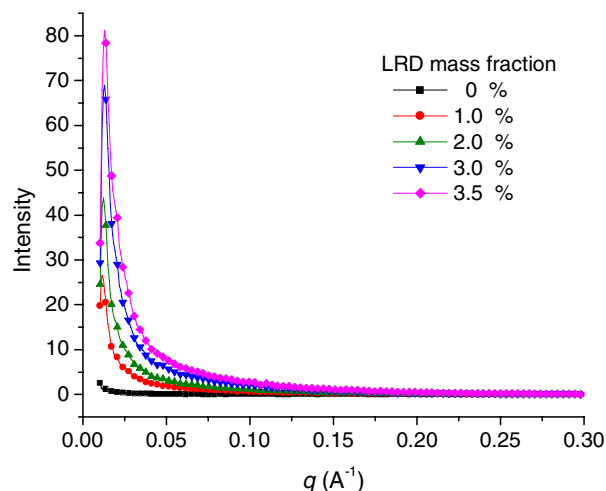
Time-resolved simultaneous synchrotron small-angle X-ray scattering and wide-angle X-ray diffraction measurements, SAXS/WAXD, were performed at the Advanced Polymers Beamline, X27C, in National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL). The wavelength of the X-ray beam was 1.366 Å. The beam size was 0.4 mm in diameter at the sample position. Synchrotron X-rays were collimated using a three 2° tapered tantalum pinhole collimator. SAXS/WAXD profiles were recorded by two linear position sensitive detectors (European Molecular Biological Laboratory, EMBL), with sample-to-detector distances of 1788 mm for SAXS and 220 mm for WAXD, respectively. The SAXS scattering angle was calibrated with silver behenate and the intensity was normalized by

incident beam fluctuations and calibrated with a LUPOLLEN standard. The relatively standard uncertainty for SAXS/WAXS measurements is 5 %.

## RESULTS AND DISCUSSION

Stable, isotropic solutions prepared using poly(ethylene oxide) and LRD from hereon will be referred to as PEO/LRD and the number following it will correspond to the clay mass fraction. Within these compositions, liquid-like to gel-like behaviors can be achieved by adjusting the clay contents. In the current study we examine the dynamics and relaxation behaviors of PEO/LRD solutions.

Small angle x-ray scattering measurements were used to verify the dispersion of polymer and clay in water (Figure 1). The intensity increased with increased clay content. Well-dispersed clay scatters strongly at low  $q$  regions but the lack of additional peaks confirms that the clays are exfoliated. WAXS intensity (not shown) was dominated by amorphous scattering and the patterns for solutions with and without clay are identical.



**Figure 1.** Small angle x-ray scattering of PEO/LRD solutions measured at 20 °C

From a Guinier analysis an apparent  $R_g$  value was calculated for each composition (Table 1). Since the polymer chains are entangled and they interact and cluster around the clay platelets, we do not assume that the  $R_g$  of a single chain could be detected. Since the  $R_g$  deduced from the Guinier analysis actually represent the second moment of the density fluctuation, we attribute this to dimension of PEO/LRD clusters. As expected, the  $R_g$  value decreased as the clay content increased since the amount of PEO chains per each laponite platelet is decreased.

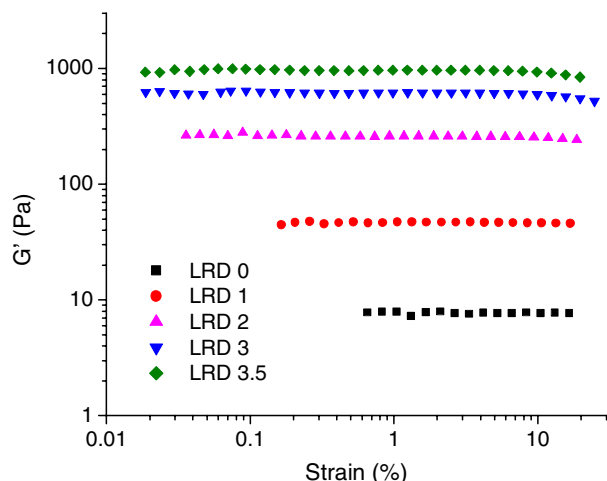
**Table 1.  $R_g$  of PEO/LRD Solutions**

Sample	$R_g$ (Å)
PEO/LRD1	137
PEO/LRD2	134
PEO/LRD3	122
PEO/LRD3.5	117

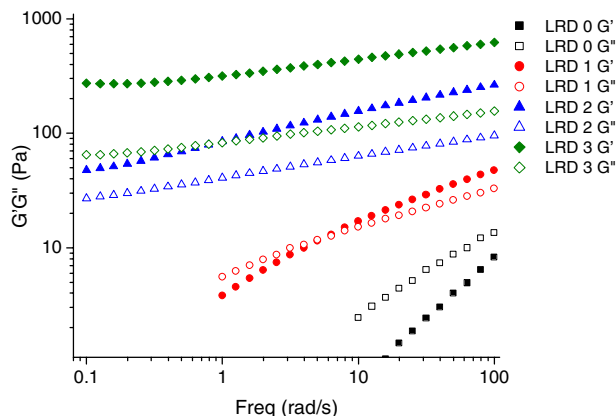
Strain sweep experiments were performed to determine the limiting strain ( $\gamma$ ) for linear viscoelastic (LV) response (Figure 2). Oscillatory experiments were performed at  $\gamma = 2$  %, ensuring LV response in frequency sweep experiments, where the frequency ( $\omega$ ) dependent complex modulus,  $G^*(\omega) = G'(\omega) + iG''(\omega)$  ( $G'$  and  $G''$  are the storage and loss moduli, respectively), was measured for PEO/LRD solutions with varied clay content (Figure 3). Pure PEO solution (without clay) showed terminal response associated with a liquid, with a terminal relaxation time shorter than 0.01 s. Upon addition of 1 % clay

\* Certain commercial materials and equipment are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation by the National Institute of Standards and Technology nor does it imply that the material or equipment identified is necessarily the best available for this purpose.

(PEO/LRD1), the terminal time of the PEO chains became accessible to the experimental frequency window, and is 0.18 s. This suggests that the addition of clay retards the longest relaxation of the PEO chains, due to the formation of associations between PEO and clay molecules. PEO/LRD solutions with higher clay contents did not show terminal relaxation (as evidenced by the low frequency crossover of  $G'$  and  $G''$ ) at  $\omega$  as low as 0.1 rad/s. The effect of formation of associations between polymer chains and clay molecules becomes more pronounced with increased clay content. At clay mass fraction of 3 %, the response of the system resembles that of a weak physical gel, as  $G'$  and  $G''$  both appear to become nearly independent of  $\omega$  in the  $\omega$  range investigated.



**Figure 2.** Dependence of  $G'(\omega)$  on  $\gamma$  at  $\omega = 100$  rad/s



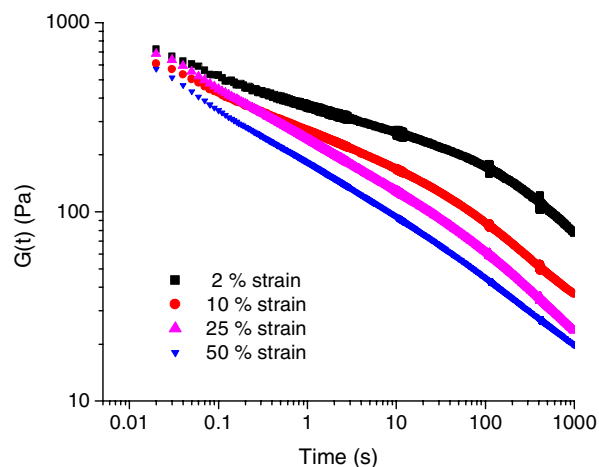
**Figure 3.**  $G'(\omega)$  and  $G''(\omega)$  for clay/polymer systems

The scaling exponent ( $n$ ) characterizing the power-law dependence of  $G'$  on  $\omega$  is listed in Table 2. The exponent for PEO solution without clay is 1.09, deviating significantly from the expected terminal zone slope of 2, possibly due to polydispersity effects. The scaling exponent of PEO/LRD1 decreased to 0.95, but the response of this system is still that of a viscoelastic liquid. The behavior of solutions containing 3 % clay is strikingly different from those containing 1 % clay. For the 3 % solutions, the response resembles that of a weak physical gel. A plateau in  $G'$  and  $G''$  at small  $\omega$  suggests the formation of a network due to the physical association between PEO chains and clay particles.

**Table 2. Scaling Exponent ( $n$ ) of PEO/LRD Solutions**

Sample	$n$
PEO/LRD0	1.09
PEO/LRD1	0.95
PEO/LRD2	0.25
PEO/LRD3	0.059
PEO/LRD3.5	0.042

Stress-relaxation experiments, which characterize the system response to a step strain, were performed to measure the stress relaxation modulus,  $G(t)$  of PEO/LRD3 solution at various strains (Figure 4). The relaxation modulus at small strains ( $\gamma = 2$  %) showed a stretched-exponential slow decay of  $G(t)$ . At these small deformations, chains are stretched in the flow direction but the network essentially remains intact. At higher strains ( $\gamma = 10$  %, 25 % and 50 %)  $G(t)$  shows highly nonlinear response, as seen by a drop in  $G(t)$  at short times. The effect of large strain amplitude is to induce extra relaxations at short times, which lower the modulus. This is likely due to disruption of the associations between the PEO chains and the clay platelets, and faster relaxations of PEO chains due to large strain amplitudes (non-linear effects).



**Figure 4.** Stress relaxation of PEO/LRD3 measured at various strains

In summary, we observe that the addition of clay to aqueous PEO solutions changes the rheological response of these systems from viscoelastic liquids at small clay concentrations to weak gels at larger clay concentrations. Current work is focused on determining the characteristic timescale of associations between the PEO chains and clay particles, along with the temperature dependence of the relaxations in these systems.

## ACKNOWLEDGEMENTS

X-ray experiments were carried out at the National Synchrotron Light Source, Brookhaven National Laboratory, which is supported by the U.S. Department of Energy. The authors would like to thank Dr. George Zhigang Wang and Dr. Jack Douglas for helpful discussions and Dr. Lizhi Liu for his support at the x-ray beam line.

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